

The rotational spectrum of chloryl chloride, ClClO_2 , in its ground vibrational state

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Rotational spectra of the four main isotopomers of ClClO_2 which together span the quantum numbers $10 \leq J \leq 77$ and $0 \leq K_a \leq 34$ have been studied in selected regions between 10 and 417 GHz. The *in situ* syntheses using reactions between FClO_2 and either HCl or BCl_3 are described. Rotational and centrifugal distortion constants have been derived and used for structure and harmonic force field calculations. The quadrupole coupling constants for both Cl nuclei have been determined and the molecular dipole moment has been derived from low field Stark effect measurements in the submillimeter region. The results are discussed in relationship to published results from a matrix-isolation study, from theoretical calculations, and from studies of related molecules.

I. INTRODUCTION

Chlorine oxides are important intermediates in the atmospheric degradation of chlorofluorocarbons and other chlorine-containing compounds leading to catalytic ozone destruction. Molina and Molina¹ proposed a catalytic cycle involving the ClO dimerization as playing a key role in the formation of the Antarctic ozone hole. They considered two possible products, dichlorine peroxide, ClOOCCl , and chlorine chlorite, ClOClO ; they suggested that only the former would contribute to net ozone loss. *Ab initio* calculations yielded three minima on the Cl_2O_2 potential energy surface,² and high level calculations indicate chloryl chloride, ClClO_2 , and ClOOCCl to be of similar stability, whereas ClOClO is approximately 40 kJ mol^{-1} less stable.³

Birk *et al.*⁴ observed the rotational spectra of the products of the ClO self reaction carried out in He at 220 K and total pressures of about 4 Torr. They found ClOOCCl as only identifiable dimer product under those conditions and they derived its structure. Soon thereafter, Müller and Willner succeeded in the synthesis of ClClO_2 . They used IR and UV/vis spectroscopy to characterize this molecule in rare gas matrices⁵ and in the gas phase,^{5,6} determined its structure using isotopic shifts of ν_5 and ν_6 , and calculated its harmonic force field. Vibrational spectra and the photochemistry of all three Cl_2O_2 isomers isolated in Ar matrices were reported by Jacobs *et al.*⁷

More recently, the formation of ClClO_2 was reported in the ClO self reaction on ice⁸ and in the photochemistry of OCClO in ice⁹ and on ice.¹⁰ These findings were taken as indications that ClClO_2 may be formed in the heterogeneous processes taking place in and on polar stratospheric cloud particles.

The initial experiments to record its microwave spectrum were carried out at the University of Tübingen in conjunction with the work reported in Refs. 5 and 6, but an assignment was not achieved. The rotational spectrum of ClClO_2 was later studied at the Jet Propulsion Laboratory (JPL) as part of a program to provide a microwave to submillimeter spectroscopic data base of molecules potentially important in the upper atmosphere¹¹⁻¹³ and to determine molecular properties that may influence chemical behavior.

Preliminary results obtained at JPL on the submillimeter spectra of the three most abundant isotopomers of ClClO_2 and a derived structure have been published previously.¹⁴ This study utilizes additional millimeter and submillimeter data as well as assignments of the initial Tübingen data. Spectra of the four main isotopomers of ClClO_2 in their ground vibrational states have been fit. An extensive set of rotational and centrifugal distortion constants are reported as well as the nuclear quadrupole coupling constants for both Cl nuclei and the molecular electric dipole moment. Ground-state effective, average, and equilibrium structural parameters as well as the harmonic force constants were derived from these data and those of earlier studies.^{5,6}

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II. EXPERIMENTAL DETAILS

Caution ! Although no explosion occurred in the course of our studies, ClF_3 , OCIO , and FCIO_2 should be handled only with proper safety precautions and in millimolar quantities. The contact of these substances with organic or other oxidizable material may lead to explosive reactions.

ClClO_2 is prepared best by reacting FCIO_2 with a volatile chloride *in situ* and passing the products through the absorption cell.^{5,6} At the university of Tübingen, FCIO_2 was prepared from OCIO and F_2 ,⁵ and a commercial sample of BCl_3 was used as the chloride. Roughly equivalent amounts of FCIO_2 and BCl_3 were flowed through a UV-spectrometer into the microwave absorption cell at total pressures around 2 Pa and at a cell temperature of 243 K. The strong 296 nm absorption of ClClO_2 ^{6,7} was used to optimize the flow conditions of the precursors.

The microwave spectrometer in Tübingen is a standard Stark modulated (50 kHz) spectrometer using phase-locked BWOs as sources. Spectra were recorded in the ranges 10–20 and 27–39 GHz. Initially, low J a - and c -type lines were specifically searched for, guided by various *ab initio* calculations.^{2,3,15} Because of strong OCIO lines and lines of unreacted FCIO_2 , no unambiguous assignment was made. Later, larger regions of the spectrum were recorded at a higher speed than normally used in order to achieve a large coverage of the microwave region. The accurately known frequencies of the ever present OCIO lines¹⁸ were used to correct for any offset caused by rapid scans in one direction. Although it appears that the yield of ClClO_2 was low, a significant number of transitions were eventually assigned.

At JPL, FCIO_2 was prepared from ClF_3 and KClO_3 . The reaction was carried out in a glass container at 273 K over night. In contrast to the syntheses described in Ref. 16, which were carried out in metal containers, O_2 was not a significant product in our experiments. A commercial sample of HCl was used as the chloride. The halogen exchange reaction was carried out using a flow system in which a relatively high pressure reaction region at several tens of Pascal was separated by a pinhole from the observation region which was in the 1 Pa range. This is similar to the flow systems described in Refs. 4, 17. Initial submillimeter observations showed that with this apparatus it was difficult at room temperature to achieve high yields of ClClO_2 with low consumptions of precursors. Large amounts of unreacted FCIO_2 remained even if significant amounts of OCIO were already observable because of the decomposition of ClClO_2 . Subsequently, conditions for ClClO_2 production were optimized by monitoring its strong absorption at 296 nm^{6,7} in the absorption cell used for rotational spectroscopy. It was found that at temperatures slightly below room temperature and at constant, slow flows of FCIO_2 and HCl the amount of FCIO_2 decreased while that of ClClO_2 increased much more than that of OCIO . Below ~ 250 K the amount of ClClO_2 decreased, and below ~ 240 K OCIO was the only observable product. Absorptions of HCl and HF were not monitored. Best results were obtained when approximately stoichiometric amounts of FCIO_2 and HCl were mixed in a ~ 1 m long, 2.5 cm i.d. reactor at pressures of 10–30 Pa, and the products were expanded through a ~ 1.5 mm pinhole into the 1 m long, 7.3 cm i.d. double path absorption cell. Both reactor and absorption cell were kept at ~ 255 K. The pumping speed was adjusted to keep the pressure in the absorption cell in the 1 Pa range; the residence time was of the order of 5 s. Under these conditions up to 30 % of the total pressure was due to ClClO_2 .

The spectrometer has been described by Friedl *et al.*¹⁷ Phase-locked klystrons operating near 100 GHz were used as sources. Diode detectors were used for fundamental frequencies, and a liquid He-cooled InSb hot electron bolometer was used to detect harmonics. The entire region between 378.5 and 395.0 GHz was scanned. Additional measurements were made between 94.5 and 131.3 GHz, near 290 GHz, and between 365 and 417 GHz. Two Stark plates, consisting of 0.953 m long, 54.8 mm wide, and 6.35 mm thick aluminum bars 25.4 mm apart, were mounted inside the absorption cell for dipole measurements of ClClO_2 in the submillimeter region.

In order to eliminate OCIO lines from consideration, published line positions as well as unpublished data from JPL for the (000), (010), (020), (100), and (001) vibrational state were analyzed¹⁸ and used for predictions. Lines of FCIO_2 in the reaction mixture were identified by recording each section of the spectrum both with pure FCIO_2 and with the reaction mixture. The FCIO_2 data were used with previous¹⁹ and additional measurements to obtain new and improved spectroscopic constants for its ground vibrational state.²⁰

III. RESULTS

A. Observed Spectra and Analysis

The pyramidal ClClO_2 is an asymmetric, prolate top with $\kappa = -0.7598$ for $^{35}\text{Cl}^{35}\text{ClO}_2$. It has C_s symmetry with a large dipole component along the c axis and a smaller one along the a axis.

Initial simulations of the rotational spectrum of ClClO_2 were made using the structural parameters and the harmonic force field from the matrix-isolation study⁵ to derive rotational constants and quartic centrifugal distortion constants.

Initial Cl nuclear quadrupole coupling constants [$I(^{35}\text{Cl})=I(^{37}\text{Cl})=3/2$] were taken from an *ab initio* calculation.¹⁵ Predictions and fittings of the spectra were done with Pickett's programs SPCAT and SPFIT.²¹

Recording the ClClO_2 submillimeter spectrum provides opportunities for pattern recognition that are not readily available in the MW region. Large sections of the spectrum can be recorded in comparatively short time, the strongest transitions are $^{\text{r}}R$ -type transitions in contrast to $^{\text{r}}Q$ -, $^{\text{p}}R$ -, and $^{\text{r}}P$ -type transitions, and the quadrupole patterns are in general more compact than those of the low J transitions which were sought in the original MW studies. A section of the submillimeter spectrum of ClClO_2 is shown in Fig. 1.

In the region near 400 GHz, the strongest features belong to high K_a c -type $^{\text{r}}R$ -branches. These are among the strongest transitions in the entire rotational spectrum. Because $A - (B + C)/2 \approx B + C$, some clustering of strong $^{\text{r}}R$ -type transitions with the same value of $J + 2K_a$ occurs at high K_a . This facilitates the identification of different series once one has been identified. Since ClClO_2 is a fairly asymmetric top, the spacing between two successive transitions of one branch decreases fairly rapidly with increasing J for $J \approx K_a$. This was an important criterion for assigning K_a quantum numbers to the identified sequences of transitions. In addition, the quadrupole splitting patterns are simple, but are sufficiently distinctive to facilitate the assignment. For $J = K_a$ the lines are very narrow and particularly intense. For increasing J or decreasing K_a the transitions are observable first as broad lines and later as partially resolved doublets which permitted an estimate of χ_{aa} at the terminal Cl atom. Among the three sequences first identified, one was assigned to the ground vibrational state of the main isotopomer $^{35}\text{Cl}^{35}\text{ClO}_2$ because of its intensity, and it was extended to six consecutive members. Comparison with predicted spectra and some trial fits led to the correct assignment of the $J'' = 24 - 29$ members of the $K_a'' = 16$ $^{\text{r}}R$ -branch. Because of the asymmetry of the molecule these transitions contained sufficient information for the determination of all three rotational constants which allowed the assignment of additional transitions and more precise determination of the molecular parameters. Transitions near the oblate limit ($K_c \approx J$) and Q -branch transitions ($K_a \approx 32$) often appeared as widely spaced (≥ 2 MHz) doublets. The splitting depends primarily on χ_{cc} at the central Cl and χ_{aa} at the terminal Cl, respectively. Information on the remaining diagonal quadrupole coupling constants was contained in the few transitions near 400 GHz observed as quartets.

Rotational constants of $^{37}\text{Cl}^{35}\text{ClO}_2$ and $^{35}\text{Cl}^{37}\text{ClO}_2$ were predicted from a preliminary structure which was derived from the rotational constants of the main isotopomer and an estimate of $r(\text{ClO})$. A harmonic force field calculation was performed with emphasis put on the reproduction of the quartic distortion constants of the main isotopomer in order to derive values for the monosubstituted isotopomers. Initial sextic distortion constants were taken from the main isotopomer. The calculated quartic constants were actually quite close to their final values and some lines were found within a few megahertz of the predictions for both isotopomers. The assignments proceeded in a straightforward manner with the fits first freeing the rotational constants and finally freeing the higher order terms after a substantial number of lines had been included in the fits. Fewer transitions were observed for the isotopomers with one ^{37}Cl than for $^{35}\text{Cl}^{35}\text{ClO}_2$ due to their factor of ~ 3 lower abundance.

Spectroscopic constants $C_{37,37}$ of $^{37}\text{Cl}^{37}\text{ClO}_2$ were estimated by applying the changes between $^{35}\text{Cl}^{35}\text{ClO}_2$ and both $^{37}\text{Cl}^{35}\text{ClO}_2$ and $^{35}\text{Cl}^{37}\text{ClO}_2$ to the main isotopomer:

$$C_{37,37} = C_{37,35} + C_{35,37} - C_{35,35} \quad (1)$$

Some transitions were found very close to the predictions. Because of the even lower abundance of $^{37}\text{Cl}^{37}\text{ClO}_2$ still fewer transitions were observed for this isotopomer. In the final fits only the rotational constants of $^{37}\text{Cl}^{37}\text{ClO}_2$ were released, whereas all other mechanical constants were constrained as described in Eq. (1). The final values of the rotational constants A , B , and C of $^{37}\text{Cl}^{37}\text{ClO}_2$ are only about 52, 255, and 524 kHz smaller than those calculated according to Eq. (1), thus justifying its use in calculating the less well determined distortion constants.

After essentially all of the observed c -type transitions had been assigned, some a -type R -branch lines could be identified tentatively. They were found very close to the predicted frequencies and had approximately the expected intensities. Because of their high quantum numbers ($J \approx 65$) their predicted uncertainties were still several megahertz. Their assignments were confirmed by additional measurements of a -type transitions in the millimeter region which had smaller uncertainties. Inclusion of a large number of these transitions with J 's in the 50–70 range and K_a 's from 0 to 33 resulted in a significant improvement in the precision of the parameters. Finally, additional measurements were made of transitions with relatively large quadrupole splitting in order to improve the quadrupole coupling constants; an example transition is shown in Fig. 2.

All lines assigned in the Tübingen MW data had $J \geq 10$. In general, the quadrupole splitting in the MW region was better determined than the absolute line positions. This was taken into account in the combined fit of the Tübingen and JPL data.

In the course of our investigations absorptions of the Coriolis coupled $v_6 = 1$ and $v_4 = 1$ vibrational states have been identified and analyzed. These results will be presented separately.

Since the effects due to the terminal and central Cl dominate the quadrupole splitting for very high and very low K_a , respectively, it matters little which of the nuclear spin angular momenta is coupled to the rotational momentum

J first to yield the intermediate quantum number F_1 . Since the largest quadrupole constant for the terminal Cl is larger than the largest one for the central Cl, the following coupling scheme was employed:

$$J + I(\text{Cl}_t) = F_1 \quad (2)$$

$$F_1 + I(\text{Cl}_c) = F \quad (3)$$

In order to reduce the number of independent quadrupole coupling constants in the fit the isotopic ratios of the χ 's were fixed to the ratio 1.2688773²² with small, fixed corrections applied to account for inertial axes rotation with isotopic substitution. This ratio holds if vibrational effects are neglected. The inertial axis systems of $^{37}\text{Cl}^{35}\text{ClO}_2$, $^{35}\text{Cl}^{37}\text{ClO}_2$, and $^{37}\text{Cl}^{37}\text{ClO}_2$ are rotated by about 0.08, 0.17, and 0.25°, respectively, compared to the axis system of $^{35}\text{Cl}^{35}\text{ClO}_2$, as calculated from the structure. Differences from the quadrupolar axis systems to the respective inertial axis system were taken from a theoretical calculation.¹⁵ Thus, the total number of fitted quadrupole constants was reduced from 16 to 4 with no significant degradation of the quality of the fit. The isotopic corrections to the quadrupole constants were not significantly determined in trial fits where they were released.

Selected transitions of $^{35}\text{Cl}^{35}\text{ClO}_2$ are given in Table I. Statistical information describing the transitions used in the final fit of ClClO_2 is given in Table II. The complete list of lines used in the final fit, their uncertainties, as well as their positions calculated from the final set of parameters is available from the Electronic Physics Auxiliary Publication Service (E-PAPS) of the American Institute of Physics.²³ A machine-readable list of $^{35}\text{Cl}^{35}\text{ClO}_2$, $^{37}\text{Cl}^{35}\text{ClO}_2$, and $^{35}\text{Cl}^{37}\text{ClO}_2$ frequencies (without hyperfine splitting), intensities, and assignments is available online in the JPL Submillimeter, Millimeter, and Microwave Line Catalog (<http://spec.jpl.nasa.gov>).¹¹⁻¹³ The spectroscopic constants are given in Table III.

B. Dipole Moment

The Stark effect measurements were made at JPL in the submillimeter region under weak field conditions using the intensity weighted average of the unresolved Stark components. As long as the shifts of the individual Stark components were within a linewidth of the intensity weighted average, the measured shifts were proportional to the square of the applied fields.

In these experiments the polarization of the millimeter waves with respect to the applied electric field was not determined. However, the rooftop reflector used to obtain two passes through the sample also rotates the plane of polarization of the reflected radiation by 90°. Therefore, it is reasonable to assume that the Stark shifted transition contains equal contributions from the $\Delta M = 0$ and $\Delta M = \pm 1$ components. For second order Stark shifts of the energy levels of the form

$$\Delta E/\mathcal{E}^2 = A + BM^2 \quad (4)$$

the shift in frequency can be expressed in closed form as the intensity weighted average of all the Stark components. Here A and B are the Stark coefficients and \mathcal{E} is the strength of the Stark field. For the present case of equal parallel and perpendicular polarization, one obtains

$$\Delta\nu/\mathcal{E}^2 = \Delta A + \Delta B[8J(J+1) - 1]/20 \quad (5)$$

for $\Delta J = 0$ with ΔA and ΔB referring to the differences between upper and lower states and

$$\Delta\nu/\mathcal{E}^2 = \pm[\Delta A + \Delta BJ(6J+7)/20 + B_{J+1}(J+1)/2] \quad (6)$$

for a $J+1 \leftarrow J$ or $J \leftarrow J+1$ transition where $\Delta A = A_{J+1} - A_J$ and $\Delta B = B_{J+1} - B_J$. The upper sign is for $J+1 \leftarrow J$ and the lower for $J \leftarrow J+1$. For individual hyperfine transitions, F is to be used instead of J .

Because the distribution of microwave power in the sample cell is a function of frequency and not well controlled and because the applied field is not very homogeneous, the transitions which are used for calibration should be preferably in the same frequency region as those used for the dipole determination. While this method is not as accurate or precise as measurements of individual components, it is quite useful when more conventional techniques are unavailable.

The $27_{3,25} - 27_{2,26}$ transition of the ground and $v_2 = 1$ states of SO_2 ^{24,25} near 385.0 and 391.8 GHz were used for calibration. Five transitions of $\text{F}^{35}\text{ClO}_2$ ^{19,20} were used to determine its dipole moment for comparison with the previously reported values and as a demonstration of the validity of the method. The transitions are given in Table IV.

Seven transitions were used for the determination of the dipole components of $^{35}\text{Cl}^{35}\text{ClO}_2$. Taking into account that μ_a was expected to be much smaller than μ_c , two transitions depended essentially only on μ_a , three mostly on μ_c , and two on both. The transitions are described in Table V. Some of the transitions investigated appeared as doublets or quartets due to ^{35}Cl hyperfine splitting. In these cases the Stark shifts of the observed lines were averaged to yield the shifts of the whole transition. The dipole moments were calculated from a set of equations

$$\Delta\nu = (C_a\mu_a^2 + C_c\mu_c^2)\mathcal{E}^2 \quad (7)$$

where C_a and C_c are calculated from Eqs. (5) or (6) for unit dipole moment components. All shifts for all the transitions were equally weighted and fitted to Eq. (6) using the method of least squares. The Stark coefficients, field strengths, observed Stark shifts as well as the residuals from the fits are presented in Tables IV and V, too.

Although the calibration factors determined for SO_2 agree with each other to within 1%, and the scatter within each data set is small, the constraints of the experimental setup mentioned above do not justify reporting the dipole moments derived here to better than about 2%. The dipole moment components of FCIO_2 and its total value are $\mu_a, \mu_c, \mu_{\text{tot}} = 0.534$ (11), 1.647 (33), 1.731 (35) D. They are in very good agreement with the literature values of 0.551 (20), 1.632 (20), 1.723 (28) D.¹⁹ The result for ClClO_2 is $\mu_a, \mu_c, \mu_{\text{tot}} = 0.457$ (10), 1.502 (30), 1.570 (32) D. For both ClClO_2 and FCIO_2 the 2% uncertainties reported are approximately double the 1σ uncertainties derived from the scatter within each data set. Possible centrifugal distortion effects on the SO_2 , FCIO_2 , and ClClO_2 dipoles have not been taken into account as they are expected to be small compared with the experimental uncertainties.

C. Structural Parameters and Harmonic Force Field

The ground-state effective structure (r_0) of ClClO_2 was calculated using Rudolph's programs RU111J and RU115.²⁶ The structural parameters were fit to the principal planar moments which were derived from the ground-state rotational constants of all four isotopomers weighted inversely proportional to the squares of their magnitudes. Following the suggestion by Rudolph,²⁷ P_b was omitted from the fit for all but the main isotopomer. The uncertainties in Table VI reflect only those from the fit.

The r_0 structure was used for a calculation of the harmonic force field as described below. The harmonic contributions to the α constants were then derived to obtain the ground-state average structure (r_z) of $^{35}\text{Cl}^{35}\text{ClO}_2$ using Typke's program MWSTR.²⁸ Isotopic variations in r_z were accounted for using Eq. (9).²⁹⁻³¹

$$r_e = r_z - 3/2a\langle u^2 \rangle + K \quad (8)$$

$$\delta r_z = 3/2a\delta\langle u^2 \rangle - \delta K \quad (9)$$

Here $\langle u^2 \rangle$ and K are the zero-point mean-square amplitude of a given bond and its perpendicular amplitude correction, respectively, obtained from the harmonic force field. The constants a are Morse anharmonicity parameters, which were approximated by values for the respective diatomics.³² Values of 1.709 and 2.021 \AA^{-1} were used for ClCl ³² and ClO ,³³ respectively. It is assumed that isotopic variations in the ground-state average bond angles are negligible.²⁹⁻³¹

The equilibrium structure (r_e) was calculated using Eq. (8). In this model, ground-state average and equilibrium bond angles are assumed to be equal.²⁹⁻³¹ While this model yields good equilibrium values in some instances, r_e and \angle_e of the OCIO radical are smaller by ~ 0.2 pm ($\sim 33\%$ of $r_z - r_e$) and $\sim 0.08^\circ$, respectively, than the values from Eq. (8).³⁴ Errors of similar magnitude may be present in these r_e parameters and should be considered when comparing them with theoretical results. Their effect on the results of the force field calculation is unimportant. All structural parameters, both experimental and from theoretical calculations, are given in Table VI.

The harmonic force field was calculated using Christen's program NCA.³⁵ The calculated r_e structure given above was used to describe the geometry of the molecule. The force constants were defined in terms of internal coordinates. Data for ν_1 were corrected because of Fermi resonance with $2\nu_2$.⁵ Effects of anharmonicity were reduced as described in Ref. 36 by using for ω_i/ν_i a value of 1.02 for the ClO_2 stretching modes ν_1 and ν_5 and a value of 1.01 for all other vibrations. The input data were weighted inversely to the squares of their attributed uncertainties: The fundamentals of the main isotopomers were given uncertainties of 0.1 cm^{-1} , resolved isotopic shifts were given uncertainties of 0.03 cm^{-1} , except for the shifts of ν_1 and ν_6 where they were twice as large because of Fermi resonance and weakness of the band, respectively. Twenty five times the experimental uncertainties were used for the quartic centrifugal distortion constants. Since the differences between ground state and equilibrium distortion constants due to vibrational effects are difficult to evaluate, the ground state constants were used as determined. The relative weight of the distortion constants with respect to the vibrational data was chosen to ensure convergence of the fit and a satisfactory reproduction of both types of input data. The initial force field of Müller and Willner⁵ reproduced the distortion

constants quite well, with the exception of Δ_K whose absolute values were predicted almost 0.7 kHz larger than the experimental values.

The resulting force constants, previous experimental values from Müller and Willner, as well as *ab initio* and density functional theory (DFT) values are presented in Table VII. Most of the force constants are precisely determined. The largest scatters occur for f_{Rr} and the sum of $f_{r\alpha}$ and $f'_{r\alpha}$. The diagonal force constants and structural parameters of ClClO_2 and related molecules are given in Table VIII. A comparison of the input data with values calculated from the force field can be found in Table IX.

The potential energy distribution for the vibrations of ClClO_2 is very similar to that of the previous force field.⁷ A moderate change occurs for ν_2 : $0.88 f_\beta + 0.07 f_{\alpha\beta}$, a somewhat larger for ν_3 : $0.31 f_R + 0.58 f_\alpha + 0.19 f_\beta - 0.04 f_{R\beta} + 0.22 f_{\alpha\alpha} - 0.25 f_{\alpha\beta}$; only contributions larger than 0.03 are given.

IV. DISCUSSION

A. Spectroscopic constants, structure, and harmonic force field

Precise rotational and centrifugal distortion constants have been obtained for ClClO_2 . These constants have allowed the accurate prediction of ClClO_2 spectra throughout the microwave to submillimeter regions. As a result, it has been possible to review spectra taken during earlier studies of ClOOCCl ⁴ and ClOClO_2 ¹⁷ for the presence of ClClO_2 . Under the conditions described in these references ClClO_2 was not an observable product in either of those experiments previously carried out in this laboratory.

The structure of matrix-isolated ClClO_2 had been determined using the product rule in the symmetry class a'' (ν_5 and ν_6), assuming the ClO bond length from the comparison of ClO vibrations of ClClO_2 , OCClO , and FCClO_2 .⁵ As can be seen in Table VI, these parameters agree well with the present, more precise gas phase values. This demonstrates that matrix IR spectroscopy can provide reasonable structural parameters if the number of elements in the symmetry class is two or less, if matrix effects are small (e. g. in neon), and if the isotopic shifts have been determined precisely.

It is shown in Table VI that the MP2/6-31G* calculation predicted a ClCl distance that is much too long. The ClO bond length and the OCIO angle are also larger than those derived from the experimental data. When larger basis sets are employed the calculated structural parameters are in better agreement with experiment, particularly for the ClCl bond length.³ The highest level coupled cluster calculation published provided very good values for the bond angles, but the bond lengths are somewhat too long. Thus, even for the highest level *ab initio* calculations published, the agreement with experiment is only moderate. DFT calculations with hybridized functionals^{15,37,38} yielded similar agreement with experiment, as demonstrated for one example in Table VI.

The MP2/6-31G* method is frequently used to estimate thermochemical properties of molecules. ClClO_2 was predicted to be higher in energy than ClOOCCl by about 100 kJ mol⁻¹.² Extrapolations based on different methods and large basis sets predicted this difference to be $\sim 4 \pm 8$ kJ mol⁻¹.³ Thus, the computations do not distinguish to within their uncertainties which is the lowest energy form of Cl_2O_2 .

It is shown in Table VIII that the difference in the XCl bond length is much larger between ClCl and ClClO_2 than between FCl and FCClO_2 . The change is even more pronounced for the respective force constants. The larger XClO bond angle in ClClO_2 compared to FCClO_2 is probably caused by steric effects of the larger Cl atom. If electrostatic repulsion between X and O atoms was dominating this angle the situation would be opposite because F is more electronegative than Cl.

In XClO_2 the electronegative halogen lowers the electron density in antibonding orbitals of the ClO_2 group, thus shortening the ClO bond and increasing the ClO force constant. As expected, both values for ClClO_2 are between those of OCClO and FCClO_2 ; and they are somewhat closer to the latter. The smaller OCIO bond angle in the chloryl halides compared to OCClO can be explained by the smaller steric requirements of 3/2 electron pairs compared to one electron pair and one halogen atom. The OCIO angle in ClClO_2 seems to be slightly smaller than in FCClO_2 . The trends in the bending force constants are as expected.

It is demonstrated in Table IX that the present force constants reproduce the input data very well. In particular, it can be seen that Δ_K , which was poorly reproduced initially, is reproduced well.

The differences between the present and the previous experimental force constants in Table VII are mainly in f_r , f_β , and $f_{\alpha\beta}$. The *ab initio* and DFT force constants agree quite well with the experimental ones. It is interesting to note that present values for $f_{\alpha\beta}$ and $f_{R\beta}$ agree better with the theoretical values than the previous values. However, rather large differences compared to the experimental values and among the theoretical calculations, for example in some of the diagonal force constants, as well as f_{Rr} and f_{rr} , show that higher level calculations are needed to accurately describe ClClO_2 .

B. Dipole Moment

The dipole moment of ClClO_2 , its components along the inertial axes as well as along the ClCl bond and in the ClO_2 plane are shown in Fig. 3 and Table X. The latter also contains values from *ab initio* calculations and experimental data for related molecules. The direction of the dipole moment is the one suggested by theoretical calculations,^{3,15,44} in the present study, as is usually the case, only the magnitudes of the components along the principal axes were determined experimentally.

As can be seen in Table VI, the MP2/6-31G* dipole moment is twice the experimental value; even with much larger basis sets MP2 calculations overestimate the dipole moment.³ The coupled cluster and density functional theory results presented in Table X show good agreement for the dipole moment and the various components.

In the chloryl halides, the withdrawal of electron density from the ClO_2 moiety by the halogens reduce the dipole components in the ClO_2 plane compared to the OClO radical, see Table X. Since Cl is less electronegative than F it seems reasonable that the ClClO_2 value is slightly larger than the FClO_2 value. These small differences should be viewed cautiously because of the comparatively large uncertainties in the dipole components. It is interesting to note that μ_{XCl} in ClClO_2 is almost as large as in FClO_2 , an indication of a fairly ionic ClCl bond in the former molecule.

C. Nuclear Quadrupole Coupling Constants

Because of the C_s symmetry of the molecule there is only one off-diagonal quadrupole coupling constant, χ_{ac} , for each nucleus. Since it was not determined, certain assumptions have to be made in order to diagonalize the quadrupole tensors. For the terminal Cl, assumption I is that the z -axis lies along the ClCl bond; assumption II is that there is no π bonding in the ClCl bond and therefore cylindrical symmetry about the z -axis. As can be seen in Table XI, the results are fairly similar: the ClCl bond is moderately ionic, comparable to the XCl bonds in HCl and ICl ; even according to assumption I, the π character of the ClCl bond is small. DFT calculations yield diagonal coupling constants which are in good agreement with the experiment, and they indicate a situation between assumption I and II, but very close to assumption I.

It is interesting to compare the quadrupole coupling constants of OClO and FClO_2 with those at the central Cl in ClClO_2 . For this comparison, the OClO molecule was rotated so that its molecular plane is in the ClO_2 plane of the ClClO_2 molecule, and the axis through the O atoms is parallel to the b axis; the quadrupole coupling constants have been transformed accordingly and are collected in Table XII. The constants of ClClO_2 are between those of FClO_2 and those of OClO , much closer to the former. Assuming that the changes in the quadrupole coupling constants from OClO to the chloryl halides are a measure of the ionic character of the XCl bond and thus also a measure of the electron withdrawal at the central Cl, the ionic character of $\sim 1/3$ for $\text{X}=\text{Cl}$ yields an ionic character of ~ 0.45 for $\text{X}=\text{F}$ if one compares the χ_{bb} values. The slightly smaller values are obtained for the other χ_{ii} probably reflect an additional small reorientation of the field gradient in the ac symmetry plane. Parent and Gerry¹⁹ obtained an ionic character of 0.64 for the FCl bond in FClO_2 assuming the population of the $3p_b$ orbitals to be the same in FClO_2 and in OClO in an orientation analogous to the present one. Considering the assumptions made in both studies, the agreement between both values is reasonable.

As can be seen in Table XII, DFT is capable of predicting diagonal quadrupole coupling constants of the central Cl well, too; one of the principal quadrupole axes is close to the ClCl bond, see Table XII and Fig. 4.

V. CONCLUSION

The present investigation of the rotational spectrum of ClClO_2 allows the precise prediction of its spectrum in the ground vibrational state well into the submillimeter region.

The gas phase molecular structure, dipole moment, and quadrupole coupling constants have been determined experimentally for the first time. These properties provide important reference points for *ab initio* or DFT calculations which are often used to evaluate thermochemical properties of molecules. The deficiencies of the highest level *ab initio* and DFT calculations to describe the Cl_2O_2 isomers make them ideal candidates for further tests. The experimental data of ClClO_2 fit well into the series of related compounds. The good agreement between the gas phase structural parameters and those from a matrix IR study shows that matrix-isolation can be used to determine reasonable structural parameters under favorable conditions.

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- ¹ L. T. Molina and M. J. Molina, *J. Phys. Chem.* **91**, 433 (1987).
- ² M. P. McGrath, K. C. Clemmshaw, F. S. Rowland, and W. J. Hehre, *Geophys. Res. Lett.* **15**, 883 (1988).
- ³ T. J. Lee, C. M. Rohlfing, and J. E. Rice, *J. Chem. Phys.* **97**, 6593 (1992).
- ⁴ M. Birk, R. R. Friedl, E. A. Cohen, H. M. Pickett, and S. P. Sander, *J. Chem. Phys.* **91**, 6588 (1989).
- ⁵ H. S. P. Müller and H. Willner, *Inorg. Chem.* **31**, 2527 (1992).
- ⁶ H. S. P. Müller and H. Willner, *Ber. Bunsenges. Phys. Chem.* **96**, 427 (1992).
- ⁷ J. Jacobs, M. Kronberg, H. S. P. Müller, and H. Willner, *J. Am. Chem. Soc.* **116**, 1106 (1994).
- ⁸ U. Kirchner, M. Liesner, T. Bentner, and R. N. Schindler, in *Tropospheric Oxidation Mechanisms. Proceedings of the EC/EUROTRAC/GDCh Meeting*, edited by K. H. Becker (CEC, Leipzig, Germany, 1994), Air Pollution Research Report 54.
- ⁹ C. J. Pursell, J. Conyers, and C. Denison, *J. Phys. Chem.* **100**, 15450 (1996).
- ¹⁰ J. D. Graham, J. T. Roberts, L. D. Anderson, and V. H. Grassian, *J. Phys. Chem.* **100**, 19551 (1996).
- ¹¹ R. L. Poynter and H. M. Pickett, *Appl. Opt.* **24**, 2235 (1985).
- ¹² H. M. Pickett, R. L. Poynter, E. A. Cohen, M. Delitski, J. C. Pearson, and H. S. P. Müller, *Submillimeter, Millimeter, and Microwave Line Catalog*, JPL Publication 80-23, Pasadena, CA (1996), revision 4.
- ¹³ H. M. Pickett, R. L. Poynter, E. A. Cohen, M. Delitski, J. C. Pearson, and H. S. P. Müller, *J. Quant. Spectrosc. Radiat. Transfer* **60**, 883 (1998).
- ¹⁴ H. S. P. Müller and E. A. Cohen, *J. Phys. Chem. A* **101**, 3049 (1997).
- ¹⁵ D. Christen, H.-G. Mack, and H. S. P. Müller, *J. Mol. Struct.*, submitted.
- ¹⁶ K. O. Christe and C. J. Schack, *Adv. Inorg. Chem. Radiochem.* **18**, 319 (1976).
- ¹⁷ R. R. Friedl, M. Birk, J. J. Oh, and E. A. Cohen, *J. Mol. Spectrosc.* **170**, 383 (1995).
- ¹⁸ H. S. P. Müller, G. O. Sørensen, M. Birk, and R. R. Friedl, *J. Mol. Spectrosc.* **186**, 177 (1997).
- ¹⁹ C. R. Parent and M. C. L. Gerry, *J. Mol. Spectrosc.* **49**, 343 (1974).
- ²⁰ H. S. P. Müller, *J. Mol. Struct.*, submitted.
- ²¹ H. M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991).
- ²² J. H. Holloway, Ph.D. thesis, Harvard University, 1956.
- ²³ See AIP document No. E-PAPS: JCPAS ???-???? for observed frequencies of ClClO₂ used in the final fit, uncertainties, assignments, and residuals. E-PAPS document files may be retrieved free of charge from our FTP server (<http://www.aip.org/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. For further information: e-mail: paps@aip.org or fax: 516-576-2223.
- ²⁴ E. A. Alekseev, S. F. Dyubko, V. V. Ilyushin, and S. V. Podnos, *J. Mol. Spectrosc.* **176**, 316 (1996).
- ²⁵ D. Patel, D. Margolese, and T. R. Dyke, *J. Chem. Phys.* **70**, 2740 (1979).
- ²⁶ H. D. Rudolph, in *Advances in Molecular Structure Research*, edited by I. Hargittai and M. Hargittai (JAI Press, Greenwich, CT, USA, 1996), Vol. 1, Chap. "Accurate Molecular Structure from Microwave Rotational Spectroscopy", pp. 63-114.
- ²⁷ H. D. Rudolph, *J. Mol. Spectrosc.* **89**, 460 (1981).
- ²⁸ V. Typke (unpublished).
- ²⁹ K. Kuchitsu, *J. Chem. Phys.* **49**, 4456 (1968).
- ³⁰ K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.* **1**, 463 (1968).
- ³¹ K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.* **4**, 41 (1969).
- ³² K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Jpn.* **38**, 805 (1965).
- ³³ J. B. Burkholder, P. D. Hammer, C. J. Howard, A. G. Maki, G. Thompson, and C. Chackerian, Jr., *J. Mol. Spectrosc.* **124**, 139 (1987).
- ³⁴ H. S. P. Müller, C. E. Miller, and E. A. Cohen, *J. Chem. Phys.* **107**, 8292 (1997).
- ³⁵ D. Christen, *J. Mol. Struct.* **48**, 101 (1978).

- ³⁶ H. S. P. Müller and H. Willner, J. Phys. Chem. **97**, 10589 (1993).
³⁷ T. Fängström, D. Edvardsson, M. Ericsson, S. Lunell, and C. Enkvist, Int. J. Quantum Chem. **66**, 203 (1998).
³⁸ Y.-K. Han, K. H. Kim, Y. S. Lee, and K. K. Baek, J. Mol. Struct. (THEOCHEM) **431**, 185 (1998).
³⁹ A. G. Robiette, C. R. Parent, and M. C. L. Gerry, J. Mol. Spectrosc. **86**, 455 (1981).
⁴⁰ R. E. Willis Jr. and W. W. Clark III, J. Chem. Phys. **72**, 4946 (1980).
⁴¹ H. Bürger, P. Schulz, E. Jacob, and M. Fahnle, Z. Naturforsch. Teil A **41**, 1015 (1986).
⁴² A. J. Downs and C. J. Adams, *The Chemistry of Chlorine, Bromine, Iodine, and Astatine* (Pergamon Press, Oxford, 1975).
⁴³ K. Tanaka and T. Tanaka, J. Mol. Spectrosc. **98**, 425 (1983).
⁴⁴ T. J. Lee, personal communication.
⁴⁵ E. W. Kaiser, J. Chem. Phys. **53**, 1686 (1970).
⁴⁶ E. Herbst and W. Steinmetz, J. Chem. Phys. **56**, 5342 (1972).

FIG. 1. Section of the submillimeter spectrum of ClClO_2 . Lines of $^{35}\text{Cl}^{35}\text{ClO}_2$ in the ground, $v_4=1$, and $v_6=1$ vibrational states are marked by 0, 4, and 6, respectively. The quantum numbers $J'_K \Omega_K \Lambda - J''_K \Omega_K \Lambda$ are given in Table I for the ground vibrational state. §, †, and ‡ indicate more than one transition of ClClO_2 , a transition of OClO and FClO_2 , respectively. Some lines show quadrupole splitting due to the Cl nuclei.

FIG. 2. The $13_{11,3} - 13_{10,3}$, $13_{11,2} - 13_{10,4}$ prolate paired transitions of $^{35}\text{Cl}^{35}\text{ClO}_2$ showing quadrupole splitting due to both terminal (upper) and central Cl (lower) as indicated. The smallest splitting (< 210 kHz) was not resolved. The quantum numbers $F'_1, F' = F''_1, F''$ are given in Table I. The strong line in the middle, marked with †, is due to OClO .

FIG. 3. Dipole vector for the ClClO_2 molecule and the dipole contributions along the ClCl bond and in the O_2Cl plane. A projection into the C_s symmetry plane of the molecule is used. The inertial axes are also shown.

FIG. 4. The principal quadrupole axes of ClClO_2 in the C_s symmetry plane according to DFT calculations; the y axes are perpendicular to the plane. The axes x' and z' were obtained under the assumption that the principal quadrupole tensor at the terminal Cl is cylindrically symmetric, i. e. there is no π bonding in the ClCl bond; further details are given in Sec. IV C

TABLE I. Observed frequencies (MHz), assignments, uncertainties^a (kHz), and residuals (kHz) (o-c) of selected rotational transitions of $^{35}\text{Cl}^{35}\text{ClO}_2$.

assignment ^b	frequency	unc	o-c
13 ₁₁ -13 ₁₀			
11.5,10&13	131 109.826	30	-16
14.5,13&16	131 110.524	35	35
11.5,11&12	131 111.320	30	23
14.5,14&15	131 111.995	30	43
12.5,11&14	131 115.673	30	8
13.5,12&15	131 116.332	35	31
12.5,12&13	131 117.118	30	-9
13.5,13&14	131 117.746	30	-20
42 _{11,31} -41 _{10,31}			
39.5,40&39; 42.5,43&42	378 052.556	30	-12
40.5,41&40; 41.5,42&41	378 053.508	30	-32
39.5,41&38; 42.5,44&41	378 054.492	30	-29
40.5,42&39; 41.5,43&40	378 055.449	30	-43
38 ₃₆ -37 ₃₆ ^c	380 440.235	25	-20
	380 442.968	25	-15
33 ₁₄ -32 ₁₃	378 520.992	60	-16
53 ₃₁ -53 ₃₀	378 534.929	50	24
59 ₂₇ -58 ₂₇	378 570.352	60	64
25 ₁₇ -24 ₁₆	365 934.286	25	-14
26 ₁₇ -25 ₁₆ ^c	372 289.805	30	-13
	372 290.717	30	-1
27 ₁₇ -26 ₁₆	378 640.374	60	14
28 ₁₇ -27 ₁₆ ^c	384 983.395	35	-43
	384 984.329	35	19
21 ₂₁ -20 ₂₀	390 432.268	35	11
23 ₂₀ -22 ₁₉	390 686.250	50	-6
25 ₁₉ -24 ₁₈	390 930.532	60	16
27 ₁₈ -26 ₁₇	391 320.084	60	15
29 ₁₇ -28 ₁₆	391 393.720	60	2
30 ₁₇ -29 ₁₆ ^c	397 647.734	35	-3
	397 648.632	35	57
50 ₃₄ -50 ₃₃	416 906.320	50	-3
20 _{5,16} -19 _{5,15}	129 760.136	30	-11
20 _{6,15} -19 _{6,14}	130 305.469	30	-1
23 ₂₃ -22 ₂₂	130 506.179	15	-5
64 ₂₇ -63 ₂₇	411 099.802	40	26
65 ₃₃ -64 ₃₃	415 640.462	80	-7
73 ₇₁ -72 ₇₀	416 925.227	60	21

^a1 σ confidence level.

^b $J'_{K'_a K'_c} - J''_{K''_a K''_c}$ K_c , K_a has been omitted for prolate and oblate paired transitions, respectively; for the oblate paired transitions K_c is preceded by a comma. F'_1, F'' quantum numbers are given in some instances; F'' quantum numbers belonging to the same F'_1 are separated by &; F'_1, F' is given by $F'_1 - F''_1 = F' - F'' = J' - J''$.

^cQuadrupole splitting; the quantum numbers F_1, F have been omitted for clarity.

TABLE II. Number of rotational levels^a and range of J and K_a quantum numbers for a - and c -type transitions, respectively, used in the final fit of ClClO_2 .

	$^{35}\text{Cl}^{35}\text{ClO}_2$	$^{37}\text{Cl}^{35}\text{ClO}_2$	$^{35}\text{Cl}^{37}\text{ClO}_2$	$^{37}\text{Cl}^{37}\text{ClO}_2$
N_{rot}^a	39	13	19	1
$J_{\text{min}}^a - J_{\text{max}}^a$	16-73	16-70	16-70	66-67
$K_{\text{min}}^a - K_{\text{max}}^a$	0-33	0-28	0-28	4-5
$N_{\text{rot}}^c < 40 \text{ GHz}^c$	25	18	20	5
$J_{\text{min}}^c - J_{\text{max}}^c$	11-75	11-54	10-66	18-43
$K_{\text{min}}^c - K_{\text{max}}^c$	2-27	2-18	2-16	3-12
$N_{\text{rot}}^{c'} > 129 \text{ GHz}^b$	74	35	40	21
$J_{\text{min}}^{c'} - J_{\text{max}}^{c'}$	12-77	20-47	20-59	20-42
$K_{\text{min}}^{c'} - K_{\text{max}}^{c'}$	0-34	1-31	2-32	1-21

^aProlate paired or oblate paired transitions are only counted once.

^bMeasured at the Jet Propulsion Laboratory.

^cMeasured at the Universität Tübingen.

TABLE III. Spectroscopic constants^a (MHz) of ClClO_2 .

	$^{35}\text{Cl}^{35}\text{ClO}_2$	$^{37}\text{Cl}^{35}\text{ClO}_2$	$^{35}\text{Cl}^{37}\text{ClO}_2$	$^{37}\text{Cl}^{37}\text{ClO}_2$
A	9450.929 47 (61)	9449.812 1 (61)	9414.679 7 (50)	9413.510 2 (74)
B	3588.057 744 (272)	3469.592 75 (106)	3565.085 10 (98)	3446.365 39 (135)
C	2787.937 669 (289)	2715.959 64 (74)	2777.265 18 (42)	2704.763 13 (103)
$\Delta_J \cdot 10^3$	1.758 777 (146)	1.661 86 (44)	1.733 69 (33)	^b
$\Delta_{JK} \cdot 10^3$	6.502 56 (50)	6.226 1 (36)	6.452 6 (27)	^b
$\Delta_K \cdot 10^3$	-1.207 55 (139)	-0.854 4 (81)	-1.225 9 (66)	^b
$\delta_J \cdot 10^3$	0.384 970 (81)	0.354 94 (32)	0.375 609 (195)	^b
$\delta_K \cdot 10^3$	6.134 62 (80)	5.887 51 (227)	6.035 91 (210)	^b
$\Phi_J \cdot 10^9$	-0.121 (20)	-0.170 (69)	-0.134 (49)	^b
$\Phi_{JK} \cdot 10^9$	9.18 (49)	9.79 (132)	11.12 (103)	^b
$\Phi_{KJ} \cdot 10^9$	27.6 (17)	22.0 (47)	23.4 (38)	^b
$\Phi_K \cdot 10^9$	-25.9 (13)	-26.8 (55)	-18.3 (48)	^b
$\phi_J \cdot 10^9$	0.108 (11)	0.075 (49)	0.112 (29)	^b
$\phi_{JK} \cdot 10^9$	3.66 (24)	3.66 (56)	3.40 (45)	^b
$\phi_K \cdot 10^9$	160.1 (52)	171.6 (149)	171.0 (111)	^b
χ_{aa}^t	-66.738 (162)	-52.637 (128)	-65.854 (162)	-52.729 (128) ^b
χ_{bb}^t	37.671 (89)	29.688 (70)	37.671 (89)	29.688 (70)
χ_{cc}^t	29.067 (126)	22.949 (99)	29.183 (126)	23.041 (99) ^b
χ_{aa}^c	-19.322 (174)	-19.338 (174)	-15.255 (137)	-15.268 (137) ^b
χ_{bb}^c	-26.319 (93)	-26.319 (93)	-20.743 (73)	-20.743 (73)
χ_{cc}^c	45.641 (122)	45.657 (122)	35.998 (96)	36.011 (96) ^b

^aNumbers in parentheses are one standard deviation in units of the least significant figures. Watson's A reduction in the representation I'' was used. χ_{ii}^t and χ_{ii}^c refer to the nuclear quadrupole coupling constants at the terminal and central Cl, respectively. Isotopic changes for the χ_{ii} were calculated from a theoretical calculation, see Sec. III A.

^bFixed according to Eq. (1); isotopic ratios have been taken into account for the quadrupole coupling constants, see Sec. III A.

^cDerived constant; isotopic ratio fixed, see Sec. III A.

TABLE IV. Transitions, frequencies (MHz), Stark field strengths \mathcal{E} (V cm⁻¹), Stark shifts $\Delta\nu$ (kHz), and difference between observed and calculated Stark shifts (kHz) used for the redetermination of the dipole moment of FClO₂.

Transition	Frequency	Stark Coefficients	\mathcal{E}^2	$\Delta\nu$	obs-calc
22 _{12,11} - 21 _{11,11}	386824.373	$C_a = -1.3204981 \cdot 10^{-10}$	$0.1785 \cdot 10^2$	-0.009	0.001
		$C_c = -1.9808196 \cdot 10^{-4}$	$0.6151 \cdot 10^2$	-0.029	0.004
			$0.2510 \cdot 10^3$	-0.125	0.010
22 _{13,10} - 21 _{12,10}	385702.423	$C_a = -1.1979055 \cdot 10^{-8}$	$0.3063 \cdot 10^4$	-0.120	-0.015
		$C_c = -1.2675217 \cdot 10^{-5}$	$0.3374 \cdot 10^4$	-0.134	-0.018
			$0.5938 \cdot 10^4$	-0.203	0.001
21 _{16,5} - 20 _{15,5}	375848.162	$C_a = 4.6349352 \cdot 10^{-5}$	$0.2967 \cdot 10^4$	0.046	0.007
		$C_c = 2.2963686 \cdot 10^{-9}$	$0.5367 \cdot 10^4$	0.076	0.005
			$0.9315 \cdot 10^4$	0.123	0.000
21 _{16,5} - 20 _{15,5}	a		$0.1359 \cdot 10^5$	0.172	-0.008
			$0.3413 \cdot 10^4$	0.043	-0.002
			$0.5908 \cdot 10^4$	0.082	0.004
			$0.9315 \cdot 10^4$	0.134	0.011
			$0.1356 \cdot 10^5$	0.183	0.004
21 _{16,6} - 20 _{15,6}	376294.671	$C_a = -4.6355038 \cdot 10^{-5}$	$0.2977 \cdot 10^4$	-0.042	-0.003
		$C_c = -4.9685606 \cdot 10^{-9}$	$0.5908 \cdot 10^4$	-0.080	-0.002
			$0.9813 \cdot 10^4$	-0.130	0.000
			$0.1356 \cdot 10^5$	-0.170	0.009
26 _{16,11} - 25 _{16,10}	382448.751	$C_a = 1.5927958 \cdot 10^{-7}$	$0.3420 \cdot 10^4$	0.012	0.000
		$C_c = 1.3155259 \cdot 10^{-6}$	$0.5908 \cdot 10^4$	0.023	0.002
			$0.1361 \cdot 10^5$	0.052	0.003
			$0.2430 \cdot 10^5$	0.085	-0.003
			$0.3817 \cdot 10^5$	0.124	-0.014

^aTwo independent experiments were done for this transition.

TABLE V. Transitions, frequencies (MHz), Stark field strengths \mathcal{E} (V cm^{-1}), Stark shifts $\Delta\nu$ (kHz), and difference between observed and calculated Stark shifts (kHz) used for the determination of the dipole moment of ClClO_2 .

Transition	Frequency	Stark Coefficients	\mathcal{E}^2	$\Delta\nu$	obs-calc
$42_{11,31} - 41_{10,31}$	378053.085	$C_a = 0.431557 \cdot 10^{-6}$ $C_c = 0.607332 \cdot 10^{-7}$	$0.2448 \cdot 10^5$	0.005	-0.001
			$0.9866 \cdot 10^5$	0.023	0.001
			$0.1541 \cdot 10^6$	0.031	-0.004
			$0.2214 \cdot 10^6$	0.047	-0.003
			$0.3005 \cdot 10^6$	0.067	-0.001
$41_{10,32} - 40_{9,32}$	379035.047	$C_a = -0.843449 \cdot 10^{-7}$ $C_c = -0.599347 \cdot 10^{-6}$	$0.6120 \cdot 10^4$	-0.009	-0.001
			$0.2448 \cdot 10^5$	-0.037	-0.003
			$0.5517 \cdot 10^5$	-0.074	0.002
$40_{11,30} - 39_{10,30}$	380100.604	$C_a = -0.130682 \cdot 10^{-5}$ $C_c = -0.570495 \cdot 10^{-7}$	$0.2448 \cdot 10^5$	-0.017	-0.007
			$0.5517 \cdot 10^5$	-0.025	-0.003
			$0.9841 \cdot 10^5$	-0.046	-0.006
			$0.1539 \cdot 10^6$	-0.067	-0.005
			$0.2214 \cdot 10^6$	-0.097	-0.008
			$0.3007 \cdot 10^6$	-0.127	-0.006
			$0.3912 \cdot 10^6$	-0.156	0.001
$45_{10,35} - 44_{9,35}$	381180.576	$C_a = 0.154511 \cdot 10^{-7}$ $C_c = 0.379831 \cdot 10^{-6}$	$0.9601 \cdot 10^4$	0.008	0.000
			$0.3810 \cdot 10^5$	0.031	-0.002
			$0.7540 \cdot 10^5$	0.066	0.001
$38_{12,27} - 37_{11,27}$	381874.147	$C_a = -0.531763 \cdot 10^{-4}$ $C_c = -0.410952 \cdot 10^{-8}$	$0.2391 \cdot 10^4$	-0.029	-0.002
			$0.6181 \cdot 10^4$	-0.070	-0.001
			$0.9601 \cdot 10^4$	-0.102	0.005
			$0.1382 \cdot 10^5$	-0.149	0.005
$40_{12,28} - 39_{11,28}$	391987.017	$C_a = 0.144187 \cdot 10^{-4}$ $C_c = 0.407061 \cdot 10^{-7}$	$0.1589 \cdot 10^4$	0.005	0.000
			$0.6181 \cdot 10^4$	0.016	-0.003
			$0.9639 \cdot 10^4$	0.033	0.003
			$0.1382 \cdot 10^5$	0.044	0.001
			$0.2448 \cdot 10^5$	0.072	-0.004
			$0.3817 \cdot 10^5$	0.117	-0.002
$42_{10,33} - 41_{9,33}$	387263.823	$C_a = -0.515435 \cdot 10^{-7}$ $C_c = -0.915059 \cdot 10^{-6}$	$0.4185 \cdot 10^3$	-0.003	-0.002
			$0.1598 \cdot 10^4$	-0.007	-0.004
			$0.6212 \cdot 10^4$	-0.016	-0.003
			$0.9678 \cdot 10^4$	-0.020	0.000
			$0.1391 \cdot 10^5$	-0.030	-0.001
			$0.3112 \cdot 10^5$	-0.061	0.004
			$0.4755 \cdot 10^5$	-0.096	0.003

TABLE VI. Structural parameters (pm, deg.) and dipole moment (D) of ClClO_2 .

parameter	experimental			
	r_0^a	r_z^a	r_e^{ab}	matrix ^c
$r(\text{ClCl})$	219.66 (15)	219.87 (14)	219.21	222. (6)
$r(\text{ClO})$	143.67 (8)	143.90 (7)	143.68	144.0 (5)
$\angle(\text{ClClO})$	104.14 (9)	104.02 (8)	104.02	103.5 (10)
$\angle(\text{OClO})$	114.96 (10)	114.63 (9)	114.63	116.0 (5)
$ \mu $	1.570 (32)			—
	<i>ab initio</i> ^d			DFT ^d
	MP2 ^e	MP2 ^f	CCSD(T) ^g	B3LYP ^h
$r(\text{ClCl})$	245.9	226.9	227.9	224.5
$r(\text{ClO})$	146.9	144.2	146.8	145.1
$\angle(\text{ClClO})$	104.2	103.8	104.1	104.4
$\angle(\text{OClO})$	116.7	115.0	114.9	114.4
$ \mu $	3.38	2.20	1.79	1.73

^aThis work. Numbers in parentheses are one standard deviation of the fits in units of the least significant figures.

^bApproximate equilibrium parameters derived from r_z ; see Sec. III C for details.

^cReference 5.

^dEquilibrium values.

^eReference 2. Møller-Plesset calculation second order with 6-31G* basis set (double zeta type with one set of d polarization functions).

^fReference 3. TZ2Pf basis set (triple zeta with two sets of d and one set of f polarization functions; see also previous footnote.)

^gReference 3. Coupled cluster calculation with single, double, and perturbative treatment of triple excitations. TZ2P basis set; see also previous footnote.

^hReferences 37, 15. Becke's three-parameter hybrid functional with gradient-corrected correlation functional of Lee, Yang, and Parr. A 6-311+G(2df) basis set was used (triple zeta with one set each of diffuse s and p functions as well as two sets of d and one set of f polarization functions).

TABLE VII. Harmonic force constants^a (N m^{-1}) of chloryl chloride, ClClO_2 .

	exptl.		theoretical ^b		
	this work	matrix ^c	CCSD(T) ^d	MP2 ^e	B3LYP ^f
f_R	119.4	124.6	112.9	105.3	119.5
f_r	852.1	816.7	727.0	1016.5	806.5
f_α	120.6	117.5	106.1	113.5	116.0
f_β	190.3	170.2	176.7	197.4	188.6
f_{Rr}	-5.8	-13.5	-5.4	-16.4	9.8
$f_{R\alpha}$	1.2	-1.1	-1.5	-2.0	-1.4
$f_{R\beta}$	-12.3	-4.2	-11.7	-15.7	-11.7
f_{rr}	-26.3	-26.3	-24.3	15.4	-14.9
$f_{r\alpha}$	3.2	3.4	-3.3	-10.8	-7.6
$f'_{r\alpha}$	-2.3	-10.1	-6.8	0.1	-1.7
$f_{r\beta}$	12.3	5.7	5.9	12.7	10.0
$f_{\alpha\alpha}$	45.1	41.2	40.5	44.0	43.7
$f_{\alpha\beta}$	40.3	10.2	36.8	40.4	40.7

^aCalculated in internal coordinates $R = r(\text{ClCl})$, $r = r(\text{ClO})$, $\alpha = \angle(\text{ClClO})$, and $\beta = \angle(\text{OClO})$; for further details on the calculation of the force field can be found in Sec. III C.

^bSee footnotes in Table VI.

^cReference 5.

^dReference 3.

^eReference 3. A TZ2Pf basis set was used.

^fReference 15.

TABLE VIII. Structural parameters (pm, deg.) and diagonal force constants (N m^{-1}) of ClClO_2 and related molecules.

	FCIO_2^a	ClClO_2^b	OClO^c	FCI^d	ClCl^e
r_{XCl}	169.07	219.21		162.83	198.8
r_{ClO}	141.99	143.68	146.98		
$\angle(\text{XClO})$	101.69	104.02			
$\angle(\text{OClO})$	115.03	114.63	117.40		
f_{XCl}	236.2	119.4		445.2	322.5
f_{ClO}	936.0	852.1	703.5		
f_{XClO}	156.4	120.6			
f_{OClO}	205.2	190.3	140.0		

^aReferences 39, 20 for approximate r_e structure and force constants, respectively.

^bThis work; approximate r_e structure.

^cReference 18; r_e structure.

^dReferences 40, 41; r_e structure.

^eReference 42; r_e structure.

TABLE IX. Comparison of experimental spectroscopic constants (cm^{-1} , kHz) with those calculated from the force field.

	$^{35}\text{Cl}^{35}\text{ClO}_2$		$^{37}\text{Cl}^{35}\text{ClO}_2$		$^{35}\text{Cl}^{37}\text{ClO}_2$		$^{35}\text{Cl}^{35}\text{Cl}^{18}\text{O}_2$	
	obs	calc	obs	calc	obs	calc	obs	calc
$(\Delta) \omega_1^a$	1062.84	1062.96	–	–0.07	–7.46	–7.15	–45.15	–45.23
$(\Delta) \omega_2^a$	527.73	526.01	–	–0.12	–4.08	–4.32	–20.54	–20.61
$(\Delta) \omega_3^a$	443.51	442.40	–1.15	–1.19	–7.10	–7.16	–7.84	–7.86
$(\Delta) \omega_4^a$	274.08	271.89	–4.28	–4.43	–	–0.44	–5.55	–5.60
$(\Delta) \omega_5^a$	1240.70	1240.98	–	–0.00	–13.39	–13.42	–42.31	–42.28
$(\Delta) \omega_6^a$	253.16	251.49	–1.25	–1.23	–0.78	–0.84	–10.14	–10.07
Δ_J	1.759	1.759	1.662	1.663	1.734	1.735	–	1.614
Δ_{JK}	6.503	6.500	6.226	6.229	6.453	6.449	–	5.696
Δ_K	–1.208	–1.219	–0.855	–0.860	–1.226	–1.246	–	–1.558
δ_J	0.3850	0.3849	0.3549	0.3550	0.3756	0.3757	–	0.3800
δ_K	6.135	6.015	5.888	5.772	6.036	5.923	–	5.344

^a ω_i for $^{35}\text{Cl}^{35}\text{ClO}_2$; $\Delta\omega_i = \omega_i(\text{ClClO}_2) - \omega_i(^{35}\text{Cl}^{35}\text{ClO}_2)$ else; see also text. Vibrational data of $^{37}\text{Cl}^{37}\text{ClO}_2$, $^{37}\text{Cl}^{35}\text{Cl}^{18}\text{O}_2$, and $^{35}\text{Cl}^{37}\text{Cl}^{18}\text{O}_2$ were also used in the calculation; the respective data have been omitted from the table because of little additional information.

 TABLE X. Dipole moment and dipole components (D) of ClClO_2 and related molecules.

	ClClO_2			FClO_2^a	OClO^b
	exptl. ^c	CCSD(T) ^d	B3LYP ^e	exptl.	
$ \mu $	1.570	1.793	1.732	1.722	1.792
$ \mu_a $	0.457	0.691	0.598	0.551	
$ \mu_c $	1.502	1.655	1.626	1.632	
μ_{XCl}	1.416	1.731	1.645	1.552	
$\mu_{\text{O}_2\text{Cl}}$	1.564	1.695	1.687	1.539	1.792

^aReference 19.

^bReference 43.

^cThis work.

^dReference 44. See also footnotes in Table VI.

^eReference 15. See also footnotes in Table VI.

TABLE XI. Quadrupole coupling constants^a (MHz) at the terminal Cl nucleus of ClClO₂, angle Θ_{za} between *z*- and *a*-axes (deg.), and ionic and π characters of the ClCl bond.

	ClClO ₂			HCl ^b	ICl ^c
	I ^d	II ^d	B3LYP ^e	exptl	
χ_{aa}	-66.738 (162)		-62.416	-67.609	-85.84
χ_{bb}	37.671 (89)		34.247		
χ_{cc}	29.067 (126)		28.169		
$ \chi_{ac} ^g$	17.340	29.972	18.124		
χ_z	-69.780	-75.342	-65.908	-67.609	-85.84
χ_x	32.109	37.671	31.661		
χ_y	37.671		34.247		
η_z	0.0772	0.0 ^f	0.0392	0.0	0.0
Θ_{za}	9.95 ^f	16.02	10.90		
i_c	0.36	0.33	0.40	0.39	0.23
π_c	0.03	0.0 ^f	0.015		

^a $v = 0, J = 0$.

^bReference 45.

^cReference 46.

^dThis work; differences in column I and II are due to the different assumptions made when diagonalizing the quadrupole tensor.

^eReference 15; see also footnotes in Table VI.

^fAssumed, see Sec. IV C.

^gAccording to Reference 15, $\text{sig}(\chi_{ac}^t) = -\text{sig}(\chi_{ac}^c)$; see Table XII.

TABLE XII. Quadrupole coupling constants^a (MHz) at the central Cl nucleus of ClClO₂ and angle Θ_{zc} between *z*- and *c*-axes (deg.).

	ClClO ₂		FCIO ₂ ^b	OCIO ^c
	exptl ^d	B3LYP ^e	exptl	
χ_{aa}	-19.322 (174)	-16.343	-34.901	32.516
χ_{bb}	-26.319 (93)	-24.519	-17.109	-51.842
χ_{cc}	45.641 (126)	40.862	52.009	19.326
$ \chi_{ac} ^{fg}$	5.87	5.168	18.10	
χ_z^g	46.167	41.325	55.77	
χ_x^g	-19.848	-16.806	-38.66	
χ_y	-26.319	-24.519	-17.109	
η_z^g	0.1402	0.1866	-0.3864	
Θ_{zc}^h	5.12	5.12	11.31	

^a $v = 0, J = 0$.

^bReference 20.

^cReference 18; values adjusted so that OCIO lies in the ClO₂ plane of ClClO₂.

^dThis work.

^eReference 15; see also footnotes in Table VI.

^fAccording to Reference 15, $\text{sig}(\chi_{ac}^t) = -\text{sig}(\chi_{ac}^c)$; see Table XI.

^gDerived from Θ_{zc} , χ_{cc} , and χ_{aa} .

^hTaken from B3LYP calculation.







